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Camphoroxalic Acid Derivatives.

Dissertation

Submitted to the Board of University Studies of the
Johns Hopkins University in Conformity
with the Requirements for the
Degree of Doctor of
Philosophy.

By

William Edwin Hoffman, Jr.

1905

Acknowledgment.

The author gladly avails himself of this opportunity to express his gratitude to President Ira Remsen and Professors H.M. Morse, H. C. Jones and E.B. Mathews for the valued instruction which he has received in lecture-room and laboratory.

This investigation was undertaken at the suggestion of Dr. J. Bishop Tingle, and to him the writer desires to express his thanks for his coöperation and council during its pursuit. To Dr. C.E. Waters, formerly of the Johns Hopkins University and to Dr. H.W. Doughty of the Carnegie Institution the author is indebted for valuable suggestions.

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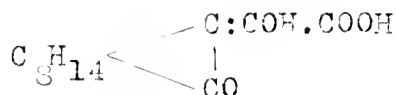
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Historical.

In 1889 J. Bishop Tingle, in the course of an investigation of the action of ethereal oxalates on aliphatic ketones, found that the impure sodium camphor obtained by the action of sodium on camphor, in boiling toluene solution, condenses with ethyl oxalate. At that time the question of the presence of the $-\text{CH}_2-\text{CO}-$ group in the camphor molecule was an open one and the first conclusive and direct proof of its occurrence was afforded by this work. Apart from the special interest which the subject thus acquired, it possessed other more general ones; hence, the investigation of the above condensation product, termed "ethylic camphoroxalate", was continued.

In 1897, to obtain light if possible on the question of the true constitution of diketones, of which camphoroxalic acid is an example. A further object was to accumulate data which might lead to a better understanding of the mechanism of the Claisen condensation. The results as regards the constitution of camphoroxalic acid are fairly complete, and indicate that it is an unsaturated ketoalcohol.

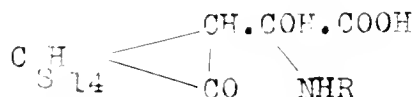
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In the course of the work, a new class of compounds was discovered, formed by the condensation of the acid with amine¹.

 1. Jour. Amer. Chem. Soc., Vol. XXIII, page 303.

The condensation compounds of the sodium and potassium salts of camphoroxalic acid and of the ethyl ester with amine¹, both aliphatic and aromatic, were studied. The primary products, in all cases, were apparently additive substances of the general type,



but only one compound of this formula could be isolated; that obtained from hydroxylamine and sodium camphoroxalate: the remainder appeared to be unstable and eliminated the elements of water, giving rise to products of the general formula:

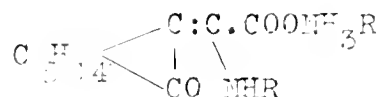


(3)

Compounds of this nature were prepared from ammonia, hydroxylamine, semicarbazine, aniline and α - and β -Naphthylamine. Such instances as those formulated above might be expected to undergo further change; carbonic anhydride might be evolved with the formation of a compound of the type:



In addition to the above a third compound of the amine with camphoroxalic acid might be formed, namely, a salt of the acid mentioned above; this would be represented by the formula



Representations of these various types were actually prepared from aniline and sodium camphoroxalate in a menthol solvent at ordinary temperatures, the second by the action of aniline and camphoroxalic acid under pressure at 130° or by heating the first compound above the melting point and the third by the action of aniline on free camphoroxalic acid in a neutral solvent at ordinary temperatures.

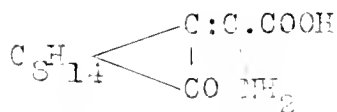
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In naming the compounds the simplest and most advisable method appeared to be to regard them as derived from the complex

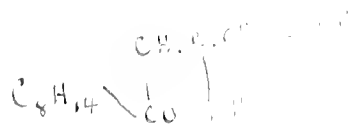
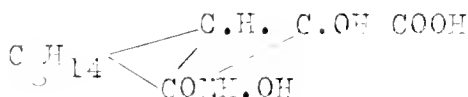


for which the term camphorformene suggests itself; it is selfexplanatory and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphoroxalate sodium or potassium camphoformene amine carboxylate was obtained from which the free acid was liberated.



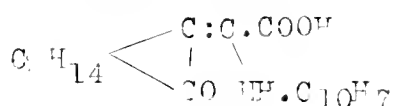
Sodium camphoroxalate combines with hydroxylamine, forming the compound



Semicarbasine combined with potassium or sodium camphoroxalate under the same conditions as hydroxylamine. The products consisted of two compounds having, apparently, the same empirical formula, but differing in their behavior toward solvents.

(5)

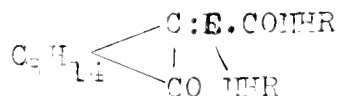
~~A~~-Naphtylamine reacted with sodium camphoroxalate under somewhat similar conditions to aniline and formed a naphtylcamphorformeneamine carboxylic acid. The corresponding derivative of ~~B~~-naphtylamine was also obtained.



The interaction of orthophenylene di amine and sodium camphoroxalate produced camphoquinoxaline, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$.

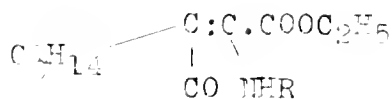
Ethyl Camphoroxalate Derivatives.

Methyl amine, ethylamine, semicarbazine, aniline and ammonia condensed with ethylcamphoroxalate to form compounds of the general formula



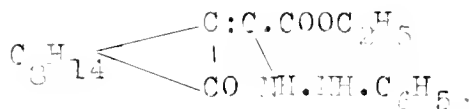
while with aniline or ~~B~~,

~~a~~-naphtylamine the product has the formula

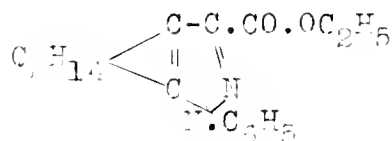


P Phenylhydrazine reacted with ethyl camphoroxalate to form

(c)



When this was treated above the melting point ethyl camphylphenylpyrazolcarboxylate results



and on hydrolyzing their compound, the free acid was obtained.

Condensation compounds could not be isolated from ethyl camphoroxalate or sodium camphoroxalate with para and meta-phenylene(diamine, ethyl aniline and dimethylaniline.

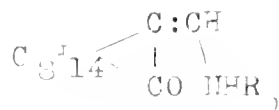
Theoretical.

The object of this investigation was to determine, if possible, what action would take place between the free camphoroxalic acid and aliphatic and aromatic amines. To ascertain, as far as possible, the limits within which the condensation takes place, to endeavor to find the cause of the inhibition of the reaction with some amines and to try to discover the conditioning factors for the production of

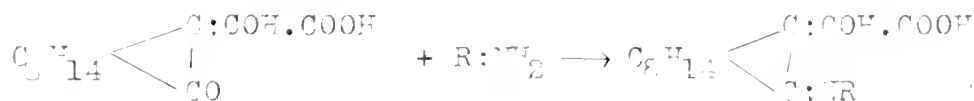
(7)

substances of the varying types referred to in the preceding pages. The action of camphoroxalic acid upon a number of metallic compounds was also investigated and the typical salts of camphoroxalic acid, described below, have been prepared and analyzed.

The third portion of this work consisted of an investigation of the action of acylhalides or substituted acylhalides upon compounds of the type

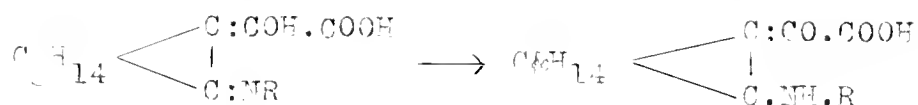


the object being to endeavor to obtain evidence of the existence in these compounds of the group R_2NH , although the behavior of hydroxylamine and of phenylhydrazine towards ethylcamphoroxalate, which has been already referred to (page 4) makes it highly probable that the amine attacks the group: $\text{C}(\text{OH})$; yet the possibility of the carbonyl group of the camphor nucleus first reacting with the amine must also be recognized. This, however, would involve the following changes



(8)

that is, the :C.OH group would remain intact and be capable of recognition, as such, which is not the case. The alternative to this is that intramolecular rearrangement might take place and result in the change



At present there is no evidence in support of this view, while the fact that, apart from the salt-forming action of the carboxyl group, camphoroxalic acid combines with amines in equimolecular proportions, would appear to be decisively against it.

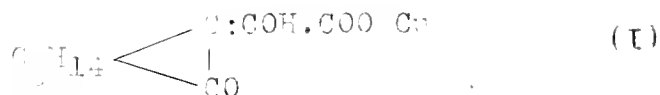
Metallic Salts of Camphoroxalic Acid.

Camphoroxalic acid was prepared by the method
1
worked out by J. Bishop Tingle.

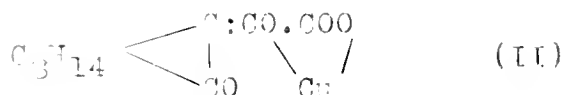
1. Jour. Amer. Chem. Soc., Vol. XXIII, p. 384.

When cupric nitrate is allowed to react with camphoroxalic acid in a solution of 50% alcohol, at ordinary temperatures, a greenish, crystalline mass is obtained, which melts and decomposes at 275° and has the formula

$C_{12}H_{14}O_4 \cdot Cu$. The product is the same, irrespective of the proportions in which the copper nitrate and acid are mixed. Two views are possible of the constitution of their salts; if the copper is present in the cuprous condition, it would be



If in the cupric state, the formula

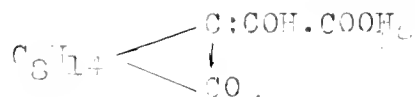


would apply, and analysis would, of course, not distinguish between them. At first sight, formula I, where the carboxyl group only is affected, would seem to be the more probable, and this view might be thought to derive support from the fact that when the salt is heated in alcoholic solution at 100° , cuprous oxide is deposited. The view that the salt is represented by formula II is based upon the following facts: its green color is characteristic of the cupric but not of the cuprous state. In solution the salt fails to give any indication of the presence of copper ions, which behavior is entirely in accordance with

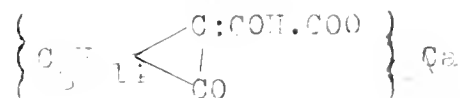
(10)

Formula II. Moreover, unlike the barium salt, this salt gives no coloration with ferric chloride and alcohol, indicating that no change has taken place in the :C.OH group of the camphoroxalic acid. The decomposition, on heating, at 100°, is doubtless analogous to that of Wehlin's solution, in which the copper is certainly in the cupric state. According to this view, the compound is a representative of a combination of two distinct types of organo-metallic derivatives, viz., the salt of a carboxylic acid and the metallic derivative of a diketone, such as the sodium derivative of ethyl acetoacetate.

When a solution of silver nitrate in 50° alcohol is allowed to react with camphoroxalic acid, a colorless silver salt is formed,

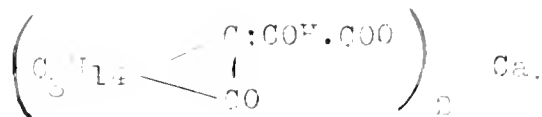


Under similar conditions barium nitrate and camphoroxalic acid form a barium salt,



Calcium nitrate reacts in the same manner, forming the calcium salt,

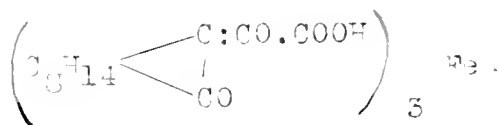
(11)



In the case of ferric chloride and camphoroxalic acid, the compound which is formed has the characteristic dark reddish violet color, which is formed in general when ferric chloride acts, in alcoholic solution, on a compound containing the enol grouping. This substance is somewhat similar to those compounds prepared by R. Schieff, in his work on the acetoacetic ester when in combination with benzylaniline.¹

1. Ber. 31, 205, 101.

Its constitution seems to be represented by the formula

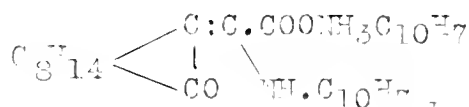


This is based on the results obtained by analysis and on the fact that the salts dissolve slowly in boiling dilute carbonate solution. It melts at about 55°.

Action of Amines on Camphoroxalic Acid.I β -Naphthylamine.—

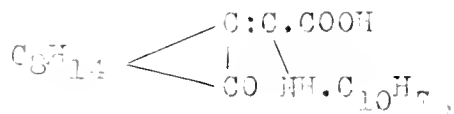
β -Naphthylamine and camphoroxalic acid yield three compounds.

1. The first of these β -naphthylamine- β -naphthyl camphoformeneamine carboxylate



is formed in hot alcoholic solution and crystallizes in slender needles of a pale yellow color, melting at 153° .

2. The second compound is obtained when this salt in very dilute alcoholic solution, is treated with sodium hydroxide and then acidified. β -naphthyl camphoformeneamine carboxylic acid,

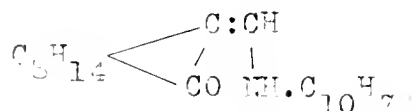


crystallizes from alcohol in slender, bright yellow needles, melting at 173.5° .

This compound has been previously described by J. Bishop
Tingle and Alfred Tingle.¹

1. Jour. Amer. Chem. Soc., Vol. XXIII, p. 375.

3. The third compound from β -naphthylamine and
camphoroxalic acid, β -naphthylcamphoformeneamine

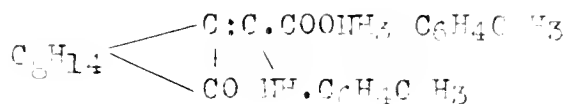


is formed by heating
either of the preceding substances above its melting point.
It crystallizes in slender, pale yellow prisms, melting at
173°.

II. Paratoluidine.—

—Paratoluidine and camphoroxalic acid
yield a series of three compounds corresponding to those
formed by β -naphthylamine.

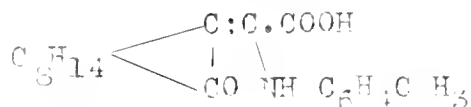
1. The paratoluidine β -tolylcamphoformeneamine
carboxylate,



is formed in alcoholic

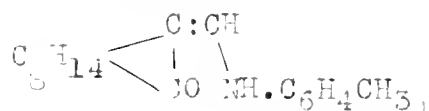
solution and crystallizes readily from alcohol in pale yellow needles, melting at 152°.

2. p-Tolylcamphoformeneamine carboxylic acid



is formed from the above salt by treatment with sodium hydroxide solution and subsequent acidification. It crystallizes from benzene as a pale yellow prisms melting at 166°.

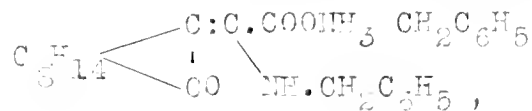
3. p-Tolylcamphoformeneamine,



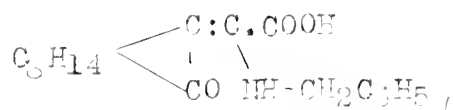
is formed by heating either of the preceding substances above its melting point. From alcohol it crystallizes in slender yellow prisms, melting at 175°.

III Benzylamine.

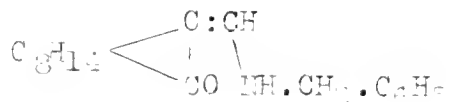
Benzylamine forms with camphoroxalic acid a series of three compounds, similar to those formed by B-Naphtylamine and p.toluidine.

1. Benzylamine-benzylcamphoformeneamine carboxylate,

is obtained by the action of the free base on camphoroxalic acid and crystallizes from alcohol in irregular rhombahedra, melting at 174°5.

2. From the above salt free benzylcamphoformeneaminecarboxylic acid,

is formed by treating it with sodium hydroxide and acidifying the resulting solution. It is a colorless compound crystallizing from ethyl acetate in clusters of fine prisms.

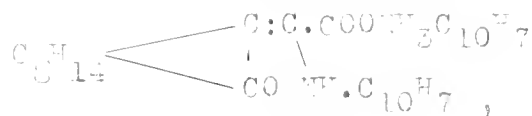
3. When heated above its melting point, each of the preceding compounds decomposes, forming benzylcamphoformeneamine

which, from alcohol, crystallizes in colorless prisms melting at 96°5

(18)

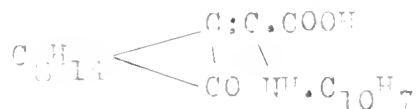
IV. α -Naphthylamine.

From α -naphthylamine and o-phthalic acid two compounds have been obtained, α -Naphthylamine Diphtaloylphoformeneazirine carbonylate,



is formed in alcoholic solution and when purified from such a solution yields greenish yellow prisms melting at 165° .

2. The above salt when heated with sodium hydroxide solution and acidified gives α -naphtholcarphoformeneazirine carboxylic acid,



which crystallizes from benzene with one-half a molecule of benzene and melts at 170° .

This acid has been described by J. Bishop Tingle and Alfred Tingle.¹

1. Jour. Amer. Chem. Soc., vol. XXIII, p. 375.

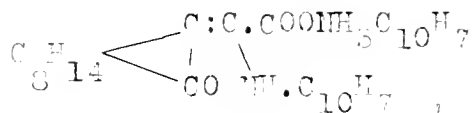
(17)

3. When heated above its melting point, each of the preceding compound, formed a viscous mass from which no compound could be isolated.

V. Metatolidine.

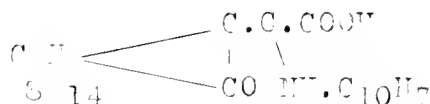
From metatolidine and camphoroxalic acid two compounds have been obtained.

1. Meta-tolidine metatolyl camphoroxalic acid carboxylate



is formed when the free acid and amine react in alcoholic solution and crystallizes from alcohol in fine needles of pale lemon color, melting at 125°.

2. The above salt when treated with sodium hydroxide solution and then acidified gives metatolyl camphoroxalic acid



which crystallizes from benzene in colorless scales, melting at 154°.

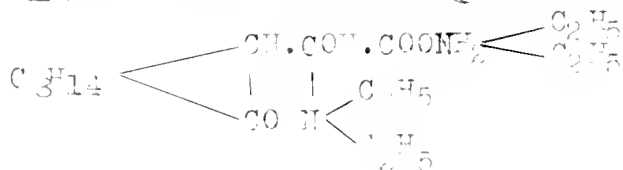
(15)

When heated above its melting point, each of the preceding compound formed a viscous mass from which no compound could be isolated.

VI. Diethylamine. —

Diethylamine and camphoroxalic acid react in alcoholic solution to form two compounds.

1. Diethylamine diethylcarbamate amine carboxylate

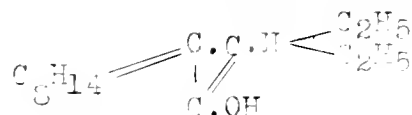


This compound crystallizes from alcohol in colorless needles melting at 139.5. It differs from the foregoing salts of camphoformeneamine (carboxylic acid) in that its formation does not involve the elimination of the elements of water, in which respect it resembles the hydroxylamine derivative previously referred to (p 4). With an alcoholic solution of ferric chloride no color reaction is produced. The term "campho-

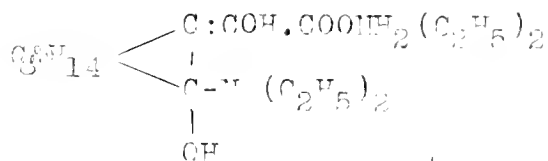
chloride no color reaction is produced. The term "carpho-
formol" is suggested for the complex $\text{C}_3\text{H}_4 \begin{matrix} \diagup & \text{C}^{\cdot}\cdot\text{COH}\cdot\text{R} \\ & | \\ & \text{CO} \quad \text{P} \end{matrix}$

It differs from camphorolene by the addition of the elements of water, one hydrogen atom being united to the camphor nucleus.

2. When this salt is heated above the melting point, it gives off water, carbondianhydride and diethylamine, and forms a compound of the same empirical formula as diethylcamphoformeneamine, $C_{15}H_{25}NO$, but which seems to differ from that substance by virtue of the fact that, with ferric chloride and alcohol, it gives the reddish violet color characteristic of the enol form, which seems to indicate that the reaction leading to its formation is hardly so simple as that which yields the corresponding derivatives of other amines. It may be possible that an isomeric compound

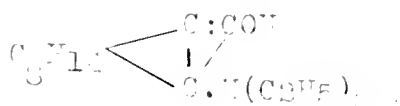


is produced or it may be that diethylamine and camphoroxalic acid yield first the compound,



which,

when heated would doubtless give a substance with the formula

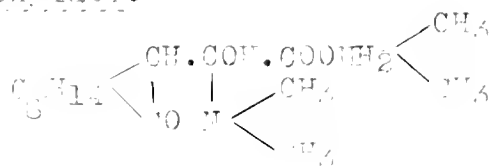


This matter will be investigated at the first suitable opportunity, as the substance in question might furnish an interesting case of dynamic isomerism.

The compound crystallizes from ethyl acetate in colorless needles, melting at 153°.

VII. Dimethylamine.

1. Dimethylamine and camphoroxalic acid, in alcoholic solution react to form dimethylamine-dimethylcamphoroxalylamine carboxylate.



which

crystallizes from acetone in colorless needles melting at 157°5. Like the corresponding compound from di-ethylamine it is apparently formed by the direct combination of acid and base without loss of a molecule of water.

2. When the salt which has just been described is heated above the melting point, it decomposes similarly to the analogous di-ethyl compound and forms a substance of the same empirical formula as di-ethylcamphoroxalylamine $\text{C}_{13}\text{H}_{21}\text{NO}$, but which, on account of the fact that it

(21)

ives a color reaction with ferric chloride, does not seem to be of that structure. It appears probable that its constitution is similar to that of the di-ethyl derivative and that its formula is

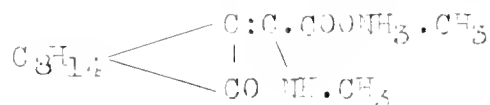


It crystallizes from alcohol in colorless needles, melting at 15°.

VIII. Netylamine.

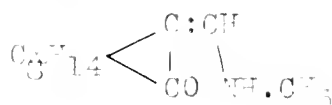
Netylamine forms two compounds with phoroxalic acid.

1. Netylamine phoroxalophoroxalanine carboxylate



which crystallizes from alcohol in slender, colorless needles, melting at 173°.

When this salt is heated above its melting point, it forms netylphoroxalanine.

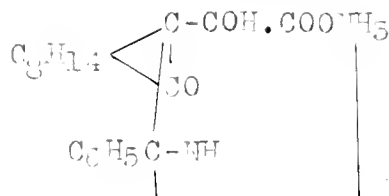


which crystallizes from

ethyl acetate in colorless needles, melting at 131°.

IX. Benzanidine.

Camphoroxalic acid in alcoholic solution, reacts with benzanidine in equimolecular proportions to form a colorless, crystalline compound, melting at 164°. At a slightly higher temperature, it decomposes to a carbonaceous mass. Dilute acids or solutions of alkalis seem to have no effect upon the compound and ferric chloride, in alcoholic solution, does not give any color reaction. The compound has the empirical formula $C_{19}H_{24}N_2O_4$. Its constitution may, perhaps, be represented by the formula

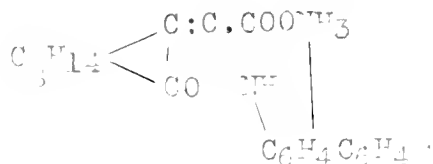


but further work will be necessary to decide this point.

X. Benzidine.

Benzidine reacts with camphoroxalic acid, in hot alcoholic solution, eliminating water and forming a greenish yellow crystalline mass, which melts at 190°, and decomposes when kept at this temperature or heated higher. The

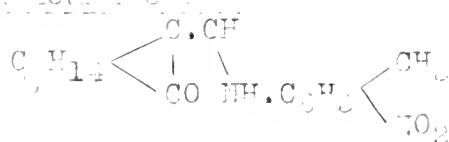
compound is apparently unchanged by the action of acids or alkalis and does not give any coloration with ferric chloride in alcoholic solution. In view of these facts and of the properties of benzidine itself, it is probable that one of the amido groups has combined with the C.OH group with the elimination of water, while the other has reacted with the carboxyl variety to form a salt, as represented by the formula



XI. 1,2,4-Nitrotoluidine.

When nitro-toluidine

($\text{CH}_3=1$; $\text{NH}_2=2$; $\text{NO}_2=4$) is heated at 150° with camphoroxalic acid, in alcoholic solution, under pressure for several hours nitro-
tolylecamphoroxalic acid is obtained.

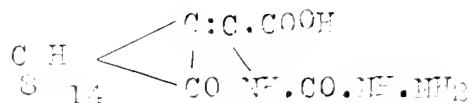


is obtained.

It crystallizes readily from alcohol in minute, bright yellow needles which melt at 192° . It was not possible to isolate the corresponding carboxylic acid or salt, although a number of experiments under varying conditions were made with this object

XII. Semicarbazine.

When semicarbazine and camphoroxalic acid react in the presence of acetic acid, a compound is formed with the composition of semicarbazine camphorformene-amine carboxylic acid.



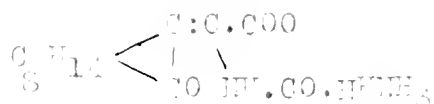
It crystallizes from alcohol in stout colorless prisms, melting at 200°. When dissolved in boiling glacial acetic acid, crystals were deposited in the form of clusters of fine needles which melt at 203°-210°. If the compound obtained from glacial acetic acid is dissolved in sodium carbonate and reprecipitated by acid, a gelatinous substance is formed which crystallizes from acetone in slender colorless needles melting at the same temperature as before, viz., 203-210°. These two substances have the same empirical formula and maintain their distinctive melting points even after heating for some time at 110°. They dissolve readily in acid sodium carbonate and are reprecipitated by acids in the form of a jelly. With alcoholic ferric chloride, a color reaction is produced in either case. All these facts lead to one of two conclusions;

either the compound or stereoisomers of the alko-fumaric type,



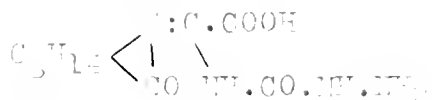
or there

is the formation of a cyclic salt



which is changed by

the glacial acetic acid into the open chain compound:



It is at present impossible to decide between these possibilities, but the problem will be more fully investigated later. Orthophenylene diamine.

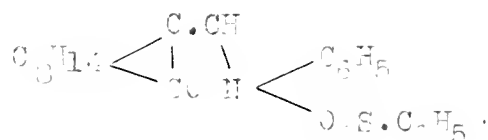
When orthophenylene diamine and camphoroxalic acid are allowed to react in a cold alcoholic solution, there is formed the camphoroxalazine compound which was prepared by J. Bishop Tighe by the action of sodium camphoroxalate and also of ethyl camphoroxalate on orthophenylene

diamine. It is a substance crystallizing from alcohol in bright yellow needles which melt at 245°. The formation of this camphorinoxaline by the interaction of sodium camphoroxalate, ethyl camphoroxalate or camphoroxalic acid, respectively, is somewhat remarkable, as it shows the tendency of this phenyldiamine derivative, in which the amine groups are in the ortho position to form a five-membered ring compound, even under conditions where we should not expect such an action to take place. Paraphenylenediamine was treated with camphoroxalic acid under the same conditions as used for the ortho compound and also under others in the hope that it might react and throw some light on this question, but no reaction product could be obtained.

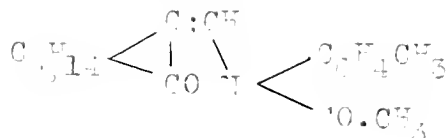
Action of Acylating Agent on Camphorformene Derivatives.

The condensation compounds from primary amines, described in the preceding pages and those previously prepared by Tingle are represented as containing an imino group. This view of their constitution was based on the nature of the compounds formed from hydroxylamine and phenylhydrazine. It is very desirable to obtain some direct evidence on this point and consequently the study of acylating agents on camphorformene derivatives was commenced. Tingle had previously shown that

with benzene sulphonyl chloride, by the Schotten-Bauman reaction, phenylcarphoformeneamine forms a compound crystallizing from benzene in colorless needles and melting at 136° , but its composition was not determined. This work was repeated and a similar compound obtained, melting at 133° , which on standing in the air soon began to decompose. It was found to be the phenylcarphoformeneaminephenylsulphone,



Acetyl chloride, when allowed to react with p. tolylcarphoformeneamine, replaces the imide hydrogen and forms acetyl p. tolylcarphoformeneamine,



which is a colorless, crystalline compound, melting at 141° . The reaction of these two chlorides with the above typical carphoformeneamines, resulting in the elimination of hydrochloric acid and the formation of the sulphone and acetyl compounds seems to be rather conclusive evidence in favor of the structure which has been ^{advanced}

For the camphoroxalates, lines 11, as we know that these bodies are formed from the corresponding carboxylic acids by the elimination of carbonic anhydride, their structure also seems to be confirmed.

Chloroacetyl chloride was allowed to react with β -naphthylcamphoroxalate, and a colorless crystalline compound was obtained, melting at 58° , unfortunately, on account of its instability, this could not be analyzed.

The following table shows the various condensation compounds of camphoroxalic acid and amines which have hitherto been prepared. They are arranged in type classes and their melting points given. The compounds marked * have been previously described by I. Bishop Tingle and Alfred Tingle.

1. Jour. Amer. Chem. Soc. vol. XXIII, p. 364.

Those marked + contain the elements of one molecule of water more than is shown in the type formula. Their constitution has been discussed only in 1921. In cases where no definite compound could be isolated, the space in the table is occupied by a dash.

FOLD OUT

Experimental.

Camphoroxalic acid was prepared according to the¹
method worked out by J. E. Tingle as follows:

1. Jour. Amer. Chem. Soc. vol. XXIII, 364.

Camphor (31.5 grams) and ethyl oxalate (22 grams) were dissolved in 400 cubic centimeters of anhydrous petroleum ether of 85°-100° boiling point and 3.5 grams of sodium wire were added. The mixture was boiled, on a water-bath, with a reflux condenser, until the violent action had ceased and the sodium almost entirely dissolved; it was then allowed to remain overnight at the ordinary temperature protected from moisture. The solution after standing was well shaken with about an equal volume of ice water and the petroleum ether extract separated from the water and dried over calcium chloride. The dried liquid was distilled, at first from the water-salts. When the temperature rises to almost 90°, the pressure is somewhat reduced and the distillation continued, care being taken not to allow the temperature of the liquid in the flask to rise above 130°; frequently it is ^{un-}necessary to heat above 120-125°.

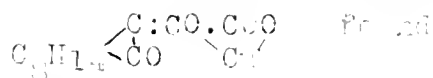
The water solution was then acidified with dilute sulphuric acid, care being taken to keep it well cooler, and then extracted three or four times with ether until a portion of the fresh ether extract shows only a pale reddish violet color with alcohol and ferric chloride. The ether was dried over calcium chloride and after filtering was distilled off and the residue added to that from the petroleum ether extract. The residue was then extracted several times by boiling with a ten per cent solution of potassium hydroxide until the filtrate, after acidification, no longer gave a marked color with alcohol and ferric chloride. This alkaline solution, from the filtered extracts, was then acidified with dilute sulphuric acid and after standing, several hours, the crystalline precipitate was filtered off. This crystalline mass was purified by recrystallization from petroleum ether, by means of a Soxhlet apparatus. The mother liquors from the recrystallizations and the residue in the Soxhlet apparatus were treated with sodium carbonate, filtered, acidified and the precipitate recrystallized.

Camporoxalic Acid Derivatives.Metallic salts of camporoxalic acid.Copper camporoxalate.—

The acid (one molecule) and copper nitrate (one-half molecule) were separately dissolved in 50% alcohol, the solutions mixed, and allowed to evaporate at the ordinary temperature, although the pure and dry copper salt does not melt below 275°. It was found that if the solution was heated on a water-bath ^{to} to remove the excess of alcohol, the green salt formed with part of the solvent an oily layer, which was extremely difficult to purify. When it is allowed to crystallize at the ordinary temperature, it is deposited as a fine green, crystalline powder which melts and decomposes at 275°. With ferric chloride, in alcoholic solution, this salt gives no coloration. If an alcoholic solution of this copper salt is heated for some time at 100°, it undergoes decomposition and deposits cuprous oxide. By analysis, this salt gave the following results:

2.1355 grams of the salt gave 1.0474 gm. of Cu_2O

Percentage calc. for



Cu

2.28

2.41

(3)

The proportions of the reacting substances were varied with the hope that another salt of different constitution might be formed, but in all cases the resulting compound was identical with the one described above.

2. Silver camphoroxalate.

Silver nitrate and camphoroxalic acid were allowed to react in a solution of 50% alcohol and, on allowing the solvent to evaporate spontaneously, a colorless, crystalline mass was obtained which was purified by repeated recrystallization from alcohol. The resulting compound was found to melt and decompose at 157°. It yielded the following results in analysis: 0.2375 gm. of the salt gave 0.0945 gm. Ag_2O .
Percentage calc. for $\text{C}_9\text{H}_{14}\text{O}_7\text{Ag}$ $\left\{ \begin{array}{l} \text{C:COO.COO} \end{array} \right.$ $\left\{ \begin{array}{l} \text{Ag.} \\ \text{found} \end{array} \right.$
A₁ 32.15 32.47

Different proportions of silver nitrate and camphoroxalic acid were allowed to react in this case also but as in the case of copper, only one compound could be isolated.

3. Barium camphoroxalate.

Barium nitrate (one molecule) and camphoroxalic acid (two molecules) in a solution of 50% of alcohol were allowed to evaporate and deposited a colorless,

(3.)

crystalline compound, which was recrystallized from alcohol. With ferric chloride and alcohol, a reddish, violet color, characteristic of the presence of the enol grouping, was found. By analysis the barium salt gave

0.1726 gr ^m of the salt gave 0.0350 Ba SO ₄			
Percentage calc. for	$\left(\text{C}_6\text{H}_{14} \begin{array}{c} \diagup \text{C:COH.COO} \\ \diagdown \text{CO} \end{array} \right)$	Ba	Found
Ba	25.51		25.21

The proportions of the reacting substances were varied, as in the preceding cases, but no other salt could be obtained.

4. Calcium camphoroxalate. —

Calcium nitrate (one molecule)

Camphoroxalic acid (two molecules) were mixed in 50% alcoholic solution, under the same conditions as in the case of the barium salt; on evaporation and recrystallization from alcohol, colorless crystals were deposited which, by analysis, gave 0.2067 gr^m of the salt gave 0.0537 Ca SO₄

Percentage	Calc. for	$\left(\text{C}_6\text{H}_{14} \begin{array}{c} \diagup \text{C:COH.COO} \\ \diagdown \text{CO} \end{array} \right)$	Ca	Found
Ca	8.20			8.4

In the case of the calcium salt also only one compound could be obtained.

5. Ferric Camphoroxalate.

Ferric chloride (one molecule) and camphoroxalic acid (two molecules) were mixed in 50% alcoholic solution. A deep reddish violet solution was produced but from no solvent could a crystalline compound be obtained, and the viscous substance, deposited by the evaporation of this solution to dryness, gave percentages of iron which showed that it had no definite composition, hence the following reaction was resorted to. The alcoholic solution of the reaction product formed from the camphoroxalic acid and ferric chloride, was diluted with water in order to precipitate any unchanged camphoroxalic acid, and at the same time to dissolve the dark red substance in solution in the alcohol. After filtering, ether was added to the liquid, but, on account of hydrochloric acid present, ~~as~~ formed by the reaction of the camphoroxalic acid and ferric chloride, it dissolved and formed a homogeneous solution with the original solution. When this mixed solution was saturated with sodium chloride and the ether took up the oil and passed and separated out the aqueous liquid, it was removed and dried over calcium chloride. The ether was then evaporated off in a water-bath. A glassy, almost black mass then remained which, by analysis, was shown

to a solution of phosphoric acid which the hydrogen at one of the
 enol group :C.OH. had been replaced by iron, while the
 carboxyl group remained intact on account of the presence
 of the hydrochloric acid during the reaction. This
 compound is soluble to a slight extent in boiling sodium
 carbonate. Analysis gave the following results:

0.2028 gr_m of ^{anhyd.} $\text{C}_{10}\text{H}_6\text{O}_2$ gave 0.0255 gr_m of Fe_2O_3

Percentage	calc. for	found
Fe	$\left(\begin{array}{c} \text{C}_{10}\text{H}_6\text{O}_2 \\ \text{CO} \end{array} \right)_3$	
	7.7.	7.6

Camphoroxalic Acid Amino Derivatives.

I. 3-Naphthylamine.

1. 3-Naphthylamine 0.4 grams (two molecules) and
 camphoroxalic acid, 1 gram, (one molecule) were mixed in
 boiling alcoholic solution which was then left at about
 100°, on a water-bath, for a few minutes. Fine yellow
 needles soon began to separate out and, on cooling, a mass
 of soft crystals was deposited. The yield was almost quan-
 titative. This compound is slightly readily soluble in hot
 alcohol and is purified by recrystallization from it. The
 purified compound crystallized in the form of fine needles

of a pale yellow color and melted at 163° with the evolution of a gas. Analysis showed it to be β -naphthylamine β -naphthyl phosphoric acid carboxylate.

0.1723 gm. of the $\text{C}_{10}\text{H}_7\text{N}$ gave 0.6 c.c. Nitrogen at 15° and 760 mm.

Percentage calc. for $\text{C}_{10}\text{H}_7\text{N} \cdot \frac{1}{10} \text{C}_6\text{H}_5\text{COOH} \cdot \frac{1}{10} \text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ found

N

5.65

5.74

This salt, when treated in alcoholic solution, with ferric chloride, did not give the violet red color characteristic of the enol grouping.

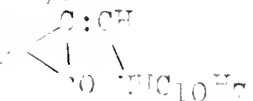
2. When the above compound is heated with a solution of sodium hydroxide, it dissolves, forming sodium β -naphthyl phosphoric acid carboxylate. On liberating β -naphthylamine, which is done it, on cooling the solution, and identified by its melting point 115° . ~~On acidification~~ ^{the} of this solution ^{was acidified} with dilute hydrochloric acid, the free β -naphthyl phosphoric acid carboxylic acid is precipitated and, after purification by recrystallization from benzene, is deposited in yellow needles melting at $172.5-173^{\circ}$. This corresponded to the melting point for the same compound prepared

1
 J. B. Tingle. This acid dissolves readily in sodium
 carbonate solution with the evolution of carbonic anhydride.

1. Jour. Amer. Chem. Soc., vol. XXIII, p. 377.

carbonate solution with the evolution of carbonic anhydride. With ferric chloride in alcoholic solution produces a red color.

3. When β -naphthyl phenylphosphonene-carboxylate is heated above its melting point, it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate when it was led into a solution of barium hydroxide. A white solid sublimes into the upper part of the tube, in which the reaction is being made, and, by its melting point, proves to be β -naphthylamine. The fused material after the evolution of gas has ceased, is purified from alcohol and crystallizes from pale yellow needles, melting at 173° . Analysis showed it to be β -naphthyl phenylphosphonene. 0.1788 g^m gave 7.1 c.c. nitrogen at 12° and 760 p.m.

Percentage calc. for $\text{C}_{19}\text{H}_{15}\text{P}$  Found

N

4.59

4.73

With ferric chloride, in alcoholic solution, a violet-red color was produced. When β -carboxyphenylcarbamoylcarboxylic acid is heated above its melting point, it gives off carbonic anhydride and forms a compound melting at 175° , identical with that formed from the β -carboxyphenylcarbamoylcarboxylic acid by heating.

LL. p-Toluidine.

Carboxyphenyl acid (1.9 grams = one molecule) and p-toluidine (4.6 grams = two molecules) were mixed in boiling alcoholic solution, which, on cooling, deposited a mass of fine yellow needles. The yield seemed to be nearly quantitative. The compound is soluble in alcohol and is purified by recrystallization from it. The purified compound crystallizes in slender, yellow needles and melts at 152° with the solution of a gas. With ferric chloride, in alcoholic solution, it gave no color reaction. Analysis corresponds to β -p-toluidine- β -carboxyphenylcarbamoylcarboxylate.

0.1616 g. of β -p-toluidine- β -carboxyphenylcarbamoylcarboxylate gave 10.2 c.c. of CO_2 at 15° and 760 mm.

Percentage = calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4$ $\left\{ \begin{array}{l} \text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4 \\ \text{O} \end{array} \right.$ $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4$ Found

g. When the above compound is heated with sodium hydroxide solution, it dissolves, forming sodium para-tolyl-carphoformene carboxylate which, on acidification, with dilute hydrochloric acid precipitates the free para-tolyl-carphoformene carboxylic acid; this is insoluble in water and has a pale yellow cast. When this substance, after re-crystallization from benzene, is deposited in yellow needles, melting at 165° with the evolution of gas. It dissolves in red fuming sulfuric acid with the liberation of carbonic anhydride and with an alcoholic solution of ferric chloride, produces no color. Analysis showed it to be Para-tolyl-carphoformene carboxylic acid.

0.1607 grm of the crd. gave 6.2 c.c. of nitroge at 6° and 740 mm.

Percentage calc. for $C_8H_7 \begin{matrix} \swarrow C:C.COON \\ \searrow NO.NH.C_6H_5.CO_2H \end{matrix}$		found
H	4.17	4.64

h. When the Para-tolylidene Para-tolylcarphoformene carboxylate is heated alone its melting point, it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate when it was led into a solution of barium hydroxide. When the tube in which the reaction

is left in allowed to cool, a crystalline white solid appears. The solid part of the liquid, by its melting point, 42° was identified as to be para-toluidine. The residue left, after the evolution of gas has ceased, is re-crystallized from alcohol and deposited in very pale yellow crystals, melting at 135°. With alcoholic ferric chloride a color is produced. Analysis showed it to be para-tolyl.

Camphoroxalic acid.

0.1710 gr. of ^{dry} ^{pure} ^{pure} gave 7.8 c.c. of nitrogen at 18° and 755 m.m.

Percentage calc. for $C_{14}H_{14}O_4$ $\begin{matrix} HO \\ \diagup \\ C \\ \diagdown \\ HO \end{matrix} \begin{matrix} CH_3 \\ \diagup \\ C \\ \diagdown \\ CH_3 \end{matrix}$ $\begin{matrix} 61.13 \\ 5.20 \\ 33.67 \end{matrix}$

When para-tolylcamphoroxalic acid is heated above its melting point, it gives off carbonic anhydride and forms a compound melting at 135°, identical with that formed by heating the para-tolyl salt of this acid.

III. Camphoroxalic acid.

1. Camphoroxalic acid (1.7 grams = one molecule) and glycine (4.6 grams = two molecules) were mixed in hot alcoholic solution and ~~after evaporation~~ ^{evaporated} part of the solvent, the water-bath, and cooling, a colorless, crystalline mass was gradually deposited. After recrystallization from

alcohol, it was obtained in the form of distorted rhombohedra melting at 147.5 with the evolution of CO_2 gas. With alcoholic ferric chloride, no color was produced. Analysis proved it to be benzylcarphor-mene-amine-carboxylate.

0.2251 gr ^{an} gave 17.7 c.c. of nitrogen at 18° and 770 m.m.

Percentage calc. for $\text{C}_8\text{H}_{11}\text{N} \begin{cases} \text{C}_6\text{H}_5\text{COO} \\ \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \end{cases}$ Found

N 7.95 ^{a solution of} 8.10

2. When the above compound is heated with sodium hydroxide solution, it dissolves, forming sodium benzylcarphor-mene-amine-carboxylate. The addition of dilute hydrochloric acid in excess to this solution produces a gummy precipitate which solidifies. After standing in contact with water and recrystallization from ethyl acetate, forms colorless crystals melting at 140°. In sodium carbonate solution, it dissolves with the evolution of carbonic anhydride and with alcoholic ferric chloride produces no color. Analysis proves it to be benzylcarphor-mene-amine-carboxylic acid.

0.035 gr of cpd. gave 0.5394 gr CO_2 and .1395 gr H_2O

(1.)

Percentage calc. for $C_8H_{11}N \begin{cases} C:O.COON \\ CO NH.CH_2C_6H_5 \end{cases}$			found
C	72.52		72.35
H	7.35		7.6

3. Heated above its melting point benzylamine hydrochlorophormeanide carboxylate gives off a gas which proves to be carbonic anhydride by the production of barium carbonate when it was passed into a solution of barium hydroxide. The fused material after the evolution of gas has ceased, is recrystallized from ethyl acetate and is deposited in colorless prisms, melting at $91^{\circ}F$. With alcoholic ferric chloride, no color is produced. Analysis showed it to be benzylaminophormeanine.
 1.66 gr of acid gave 3.6 c.c. of nitrogen at 11° and 760 m.m.

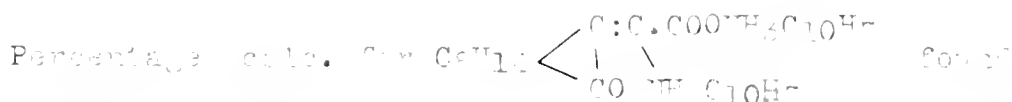
Percentage calc. for $C_8H_{11}N \begin{cases} C:OH \\ \quad \backslash \\ CO NH.C_6H_5 \end{cases}$			Found
N	1.07		1.15

If benzyl- α -phormeanic hydrocarboxylic acid is heated above its melting point, it also gives off carbonic anhydride and forms a compound melting at $91^{\circ}F$, identical with that formed by heating the benzylamine salt of the acid.

(11)

IV. α -Naphthylamine. -

Crystalline (m.p. = 115°) α -naphthylamine (0.1 gm. = two e.c.c.) was dissolved in alcoholic solution, and with the solvent, greenish yellow crystals, were ^{inc.} ~~obtained~~ which, after purification in alcohol, melt at 115°, with the evolution of gas. With ferric chloride, in alcoholic solution, no color is produced. Analysis proved it to be α -naphthylamine - carboxylic acid. 0.105 gm. of m.p. gave 7.5 e.c.c. of nitrogen at 16° C. 731 e.c.c.



N

7.5

7.3

The salt dissolves when treated with sodium hydroxide solution, forming sodium α -naphthylcarboxylate which, on acidification with dilute hydrochloric acid, forms a yellow precipitate, which, after crystallization from water, melts at 150° C. The salt is a white solid which, on the addition of sodium carbonate with the evolution of carbonic dioxide gas, with addition of ferric chloride, produces no color.

3. When either of the above α -phenyl- β -keto acids was heated, in order to obtain α -phenyl- β -keto acid derivative, a yellow substance was obtained, which could not be induced to crystallize from alcohol.

V. Meta-toluidine.

1. Carboxylic acid (7 grams = one mole) and meta-toluidine (4.5 grams = two moles) was allowed to react in alcohol solution; after evaporation, ~~the~~ was deposited fine needles of pale green color which, after recrystallized from alcohol, melted at 151° . With alcohol in ferric chloride, no color was produced. Analysis showed this substance to be meta-toluidine met-tolylcarboxylate or meta-toluidine carboxylate.

$d = 1.53$, $n_D^{20} = 1.523$, $n_D^{25} = 1.519$, $n_D^{30} = 1.515$, $n_D^{35} = 1.511$, $n_D^{40} = 1.507$, $n_D^{45} = 1.503$, $n_D^{50} = 1.499$, $n_D^{55} = 1.495$, $n_D^{60} = 1.491$, $n_D^{65} = 1.487$, $n_D^{70} = 1.483$, $n_D^{75} = 1.479$, $n_D^{80} = 1.475$, $n_D^{85} = 1.471$, $n_D^{90} = 1.467$, $n_D^{95} = 1.463$, $n_D^{100} = 1.459$.

Percentage calc. for $C_9H_9O_2$ $\left\{ \begin{array}{l} C: C.COOH \cdot C_6H_4 \cdot CH_3 \\ H: 2H.C_6H_4 \cdot CH_3 \end{array} \right.$ found

C 75.5% 75.5% H 5.5% 5.5%

2. The above salt, when treated with a solution of sodium hydroxide dissolved in water, sodium meta-tolylcarboxylate, which, on acidification, with dilute hydrochloric acid, gives a yellow precipitate. After purifi-

tion from benzene, which is deposited melting at 154°.

They dissolve in ^{a solution of} sodium carbonate ~~with~~ with the evolution of carbonic anhydride only with alcoholic ferric chloride give no color. Analysis shows it to be meta-tolylcarphos formeneamine carboxylic acid.

1497 ^{mm} ^{on mm} μ μ gave .35 c.c. of nitrogen at 10° and 770 m.m.

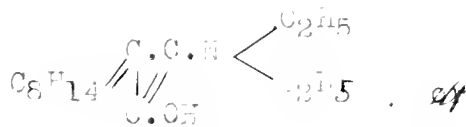
Percentage	calc. for C_8H_{11}	$\begin{array}{l} C:C.COOH \\ \quad \\ CO \quad NH \quad C_6H_4 \quad CH_3 \end{array}$	found
N	4.47		4.56

3. Both meta-tolylcarphosformeneamine carboxylic acid and its meta-tolylidene salt on heating gave a gas, which could not be obtained pure enough for analysis.

VI. Diethylamine.

(1. Camphoroxalic acid (5 grams = one molecule) was allowed to react with an alcoholic solution (3.4 grams = two molecules) of diethylamine, a compound crystallizing in colorless needles is obtained, which when purified by recrystallization from alcohol, melts at 139.5 with the evolution of a gas. With alcoholic ferric chloride, it gives no color reaction. By analysis the compound is shown to be diethylamine diethylcarphosformeneamine carboxylate.

is identical with that of diethylcamphoramine, but on account of its behavior toward ferric chloride, its constitution is probably experienced (page) to be represented by the formula:



0.2045 gr of ~~cpd.~~ gave 8.1 c.c. of nitrogen at 15° and 762 m.m.

Percentage calc. for	$\text{C}_8\text{H}_{14} \begin{array}{c} \text{C.C.N} \\ \text{//} \quad \text{//} \\ \text{C.OH} \end{array} \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array}$	found
N	4.56	4.66

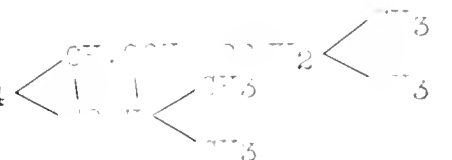
VII. Dimethylamine.

1. Camphoroxalic acid (5 grams= one molecule) and dimethylamine (2 grams= two molecules) were allowed to react in alcoholic solution and, after part of the solvent had evaporated spontaneously, a crystalline compound was obtained. After recrystallization from acetone, colorless needles were deposited, melting at 137.5° with the evolution of a gas. With alcoholic ferric chloride it produced no color reaction. Analysis showed it to be dimethylamine dimethylcamphorformol-amine carboxylate.

I. 0.2044 gr of ~~cpd.~~ gave 4.4452 gr CO₂ and 0.1661 gr of H₂O

II. 0.2135 gr of ~~cpd.~~ gave 4.816 gr CO₂ and 0.1770 gr of H₂O

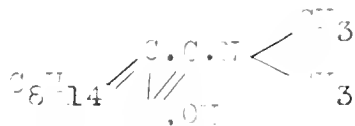
(49)

Percentage calc. for C_8H_{14}  found

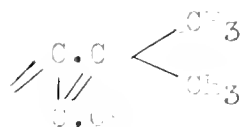
		I	II
C	61.14	60.71	61.58
H	9.55	9.29	9.27

2. When dimethylamine dimethylcamphoformolamine(carboxylate is treated with sodium hydroxide solution, it dissolves, but on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and dimethylamine.

3. When heated to 140° , di(methylamine dimethylcamphoformolamine(carboxylate gives off water, carbonic anhydride and dimethylamine, and forms a compound which, when purified by recrystallization from acetone, melts at 63° . With alcoholic ferric chloride it gives a purple color, and analytical results to the formula which might be



g 2456 gr. of cpd gave 14.8 c.c. of nitrogen at 19° and 770 m.m.

Percentage calc. for C_8H_{14}  found

N	6.77	7.01
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VIII/ Methylamine.

1. Camphoroxalic acid (5 grams= one molecule) and methylamine (2.8 grams= two molecules) were mixed in alcoholic solution. After evaporation of part of the solvent colorless needles were deposited, purified by recrystallization from alcohol and melted at 172°. With alcoholic ferric chloride no color reaction was produced. Analysis proved the compound to be methylamine methylcamphoformeneamine¹carboxylate.

0.2147 gr. of cpd. gave 20 c.c. of nitrogen at 14° and 766 m.m.

Percentage	calc. for $C_8H_{14} \begin{matrix} \swarrow \\ \text{C:O} \cdot \text{COO} \cdot \text{NH}_3\text{CH}_3 \\ \searrow \\ \text{CH} - \text{CH}_3 \end{matrix}$	found
N	10.51	11.04

2. When treated with sodium hydroxide, the above salt dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and methylamine.

3. Upon heating at 175° methylamine methylcamphoformeneamine¹carboxylate gives off methylamine and carbonic anhydride and forms a compound which ^{when} recrystallized from ethyl acetate, melts at 131°. With alcoholic ferric chloride, no color reaction is produced. Analysis proved it to be methylcamphoformeneamine.

(51)

2131 gr. of $\text{C}_6\text{H}_{14}\text{N}_2$ gave 13.3 c.c. of nitrogen at 11° and 765 m.m.

Percentage	calc. for $\text{C}_6\text{H}_{14}\text{N}_2$	$\begin{array}{l} \text{C}:\text{C}'' \\ \quad \backslash \\ \text{CO} \quad \text{NH}.\text{C}''\text{H}_3 \end{array}$	found
N	7.25		7.50

IX. Benzamidine.—

— Free benzamidine (2.2 grams= one molecule) is obtained by dissolving the hydrochloride in absolute alcohol adding the required amount of potassium hydroxide and filtering off the insoluble potassium chloride. When camphoroxalic acid (5 grams= one molecule) is allowed to react with such an alcoholic solution of benzamidine and the solvent is allowed to evaporate, a compound is obtained which may be purified by recrystallization from alcohol. It is deposited in colorless prisms; these melt at 184° , evolve a gas and decompose to a cleared mass. With alcoholic ferric chloride no color reaction is produced and neither acid nor alkali seems to cause any change in its composition. When heated above its melting point, it decomposes completely to a carbonaceous mass from which it was impossible to obtain any definite compound. It did not dissolve in sodium carbonate. Analysis proved it to be of the empirical formula, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_4$

0.2147 gr of cpd. gave 15.5 c.c. of nitrogen 19° and 766 m.m.

Percentage	calc. for $C_{19}H_{24}N_2O_4$	found
N	8.14	8.30

0.1539 gr of cpd. gave 3723 gr CO_2 and 0963 gr of H_2O

Percentage	calc. for $C_{19}H_{24}N_2O_4$	found
C	66.27	65.93
H	6.97	7.002

X. Benzidine. — >

— Camphoroxalic acid (5 grams = one molecule) and benzidine (4 grams = one molecule) were mixed in hot alcoholic solution. When cooled, this deposited a dense mass of greenish yellow microscopic needles ~~was deposited~~, which on account of its very sparing solubility in all the ordinary organic media, was extracted with ether to remove any camphoroxalic acid and benzidine, when the compound formed a fine powder, which gave no color reaction with alcoholic ferric chloride and was not affected by acids or alkalies. It melts at 190° and when heated above this temperature, it decomposed to a carbonaceous mass. It is insoluble in sodium carbonate. Analysis prove it to have the empirical

formula $C_{24}H_{26}N_2O_3$ Its possible constitution is discussed on p. —

0.1489 gr. of ~~cpdk~~ gave 9.4 c.c. of nitrogen at 21° and 775 m.m.

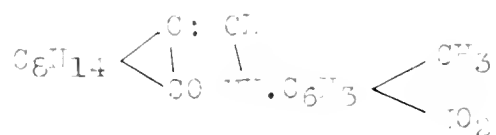
Percentage	calc. for $C_{24}H_{26}N_2O_3$	found
N	7.18	7.31

XI. Para-nitroorthotoluidine.

When camphoroxalic acid (5 grams = one molecule) and nitro~~toluidine~~ (6.8 grams = two molecules) are heated at 150° under pressure, in alcoholic solution for four hours, a yellow compound is obtained which is purified by recrystallization from alcohol. It is deposited in bright yellow needles melting at 192°. This compound is unaffected by acids or alkalis, does not dissolve in sodium carbonate and produces no color ^{reaction}

with ferric chloride in alcoholic solution. Considerable difficulty was experienced in the combustion of this substance for the determination of nitrogen, even when the heating was done most cautiously, explosions occurred so that the analytical results were unreliable. These explosions were probably due to the presence of the nitro group in the compound. The difficulty was overcome in a thoroughly sat-

isfactory manner by mixing the substance with aluminum powder; when this was done the nitrogen was evolved during the combustion in a stream which could be easily regulated. Analysis of the compound showed it to have the empirical formula $C_{18}H_{14}N_2O_3$ which agrees with the structural formula



0.2145 gr of compd gave 8.8 c.c. of nitrogen at 17° and 765m.m.

Percentage	calc. for $C_8H_{14} \begin{array}{l} \diagup C:CH \\ \\ CO \end{array} \cdot C_6H_5 \begin{array}{l} \diagup CH_3 \\ \\ CO \end{array}$	found
N	4.66	4.79

XII. Semicarbazine.

1. Semicarbazine hydrochloride (two molecules) was dissolved in as little cold water as possible and added to an alcoholic solution of potassium acetate (two molecules); this solution was then mixed with an alcoholic solution of camphoroxalic acid (one molecule. After evaporation of most of the alcohol, the solution was greatly diluted with water, a white crystalline precipitate was produced which, on

on purification by recrystallization from alcohol, formed colorless prisms, melting at 200° . When dissolved in boiling glacial acetic acid and precipitated by the addition of alcohol, clusters of colorless, microscopic needles are deposited; these melt at 209° - 210° and correspond to the compound described by Tinsle,¹ as one of two substances

1. *Jour. Amer. Chem. Soc.* Vol. **LXXIII** p. 373.
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formed by the action of semicarbazine on potassium camphor-oxalate in alcoholic solution at 100° , under pressure. The presence of a second compound described by him as being deposited from acetone in colorless needles melting at 218° could not be detected and is apparently not formed under the conditions employed by me. If the compound, melting at 209° - 210° , obtained from acetic acid solution, was dissolved in sodium carbonate solution and precipitated by acids, it formed a jelly which, after having dried and recrystallized from acetic acid, had the same melting point as before, viz., 209° - 210° . If the original compound from alcohol, melting at 200° , is recrystallized from acetone, its melting point remains constant. With alcoholic ferric chloride, neither substance produces a color reaction. Both dissolve

readily in sodium carbonate and, as has been stated, are precipitated from this solution by acids, as colorless jellies. Analysis showed that both compounds are the compositions of semicarbazine camphoformene-carboxylic acid.

0.2145⁰⁰⁰ of cpd. gave $\text{CO}_2 = 0.4373$ gr. and $\text{H}_2\text{O} = 0.1261$ gr.

Percentage calc. for $\text{C}_8\text{H}_{14} \begin{matrix} \swarrow \text{C:C.COOH} \\ \searrow \text{C:CH}_2\text{CO.H}_2\text{N} \end{matrix}$ found

C	55.6	55.5
H	6.76	6.57

The constitution and relationship of these compounds has been discussed on p.

Orthophenylene diamine.

Camphoroxalic acid (5 grams = one molecule) and orthophenylene diamine (2.4 grams = one molecule) were allowed to react in alcoholic solution. The evaporation of the solvent, fine yellow needles deposited, which melt at 246° . This substance is identical with the compound obtained by J. Bishop Tingle. The proportional quantities of the reacting

1. Jour. Amer. Chem. Soc., vol. XXIII, p. 375.

substance and the conditions of the experiment were varied, but, in all cases, the same compound was obtained.

The action of camphoroxalic acid on acetylphenylhydrazine, carbazide^m, paranitroaniline, paracetanilide, methylaniline, ethylaniline, benzylaniline, ethylenediamine, benzylphenylhydrazine, guanidine, pyridine, dimethylaniline, orthotoluidine, parabromophenylhydrazine and hydrazine was tried under conditions similar to those already described for other amines but in no case could a definite compound be obtained. The reaction products were unusually gummy substances which could not be obtained in a crystalline form. They were heated for some time at 150°-180° in the hope of forming compounds of the camphoformeneamine type, but here also no crystalline derivatives could be isolated by the use of the ordinary organic solvents.

Possibly further investigation of these compounds may result in their purification by distillation under very low pressures.

III Action of Acylating agents on Camphoformene derivatives.

Paratolylcamphoformeneamine (3 grams = one molecule) and acetyl chloride (2.6 grams = three molecules) are boiled in solution of anhydrous ether for about six hours, the ether was then evaporated off, leaving a compound which crystallized from alcohol in colorless needles, melting at 161°. Analysis

showed it to be acetyl para-tolylcamphoformeneamine.

0.1056 gr_A of the cpd_A gave 0.2992 gr_A of CO₂ and 0.735 gr_A H₂O.

Percentage calc. for $C_8H_{14} < \begin{matrix} \text{C}_6\text{H}_5\text{CH}_3 \\ \text{CO.CH}_3 \end{matrix}$ found

C 77.4 77.26

H 7.74 7.47

0.5403 gr_A cpd_A gave 0.9983 gr_A of $\text{C}_8\text{H}_7\text{P}_2\text{O}_7 = \frac{0.9747}{2} \text{C}_8\text{H}_7\text{O}$

Weight calc. for $C_8H_{14} < \begin{matrix} \text{C}_6\text{H}_5 \\ \text{CO.CH}_3 \end{matrix}$ found

$\text{C}_8\text{H}_7\text{P}_2\text{O}_7$.0964 .0983

Then phenylcamphoformeneamine was treated with phenyl sal-
phonic chloride by the Schotten-Taumann method; i.e., 1 gram=
1 molecule) phenylcamphoformeneamine was shaken with (one
gram = 7 molecules) sodium hydroxide in 10% water solution
and (3.5 gram = 5 molecules) phenyl salphonic chloride, which
were added alternately and in small quantities, a compound
is obtained which, by crystallization from benzene, is de-
posited in stout, colorless needles, melting at 155°.

Analysis shows it to be phenylcamphoformeneamine phenylsulphur .

(79)

0.1241 gr. of ~~acid~~ gave 0.1311 gr. BaCO_3 .

Percentage calc. for $\text{C}_{26}\text{H}_{14}$ $\begin{array}{c} \text{C:O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ $\begin{array}{c} \text{C:O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ found

C

8.10

8.07

3-Naphthylcamphoraneamine (2 grams = one molecule) and chloroacetyl chloride (2.1 grams = three molecules) react in anhydrous ether, when boiled for some hours to form a bright red substance which was purified by distillation under diminished pressure. It boiled at 116° under 45 mm. in pressure. It condensed to a colorless crystalline solid which could be further purified by means of petroleum ether. From this it was deposited in colorless needles melting at 66° . The compound dissolves in acid sodium carbonate with evolution of carbonic anhydride and gave no color reaction with ferric chloride. It is very unstable and consequently could not be obtained in a state of purity sufficient to give concordant results on analysis.

iographical.

William Edwin Hoffman, Junior, was born in Baltimore, Maryland, January 27, 1881. He received his early education in the Baltimore City College and after one year in Deichmann's College Preparatory School entered the Johns Hopkins University in October, 1899. After devoting the following three years to the completion of the Chemical-Geological course, he received the degree of Bachelor of Arts in June, 1902. In October, 1902 he entered the Johns Hopkins University as a student in Chemistry. His subordinate subjects have been Physical Chemistry and Mineralogy.



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